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Scanning tunneling microscopy imaging of transition-metal dichalcogenides

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Structural features of TiS_2 were studied by scanning tunneling microscopy (STM) and single-crystal x-ray diffraction was applied as a complementary technique. STM images in air and at room temperature revealed, besides the trigonal symmetry of the lattice, several new features having this symmetry as well. We conclude that these features are not only to be described by structural defect phenomena which affect sites in the 1T-CdI_2 structure but tetrahedral sites as well. Sample orientation determination by x-ray diffraction provides a unique relation between feature types and sites. A model is proposed in which displaced Ti atoms account for the observed features.

Right from the start of scanning tunneling microscopy,[1,2] graphite has become the most important prototype system since it is easy to prepare atomistically flat surfaces over considerably large areas. In addition, several layered materials such as transtion-metal dichalcogenides have been shown to be ideal scanning tunneling microscopy (STM) substrates.[3] The surfaces of these materials are expected to be very flat on an atomic scale and chemically inert. For that reason atomic resolution STM pictures can be obtained quite easily, even in air.

Here we report new features in STM observations of TiS_2 that belong to the class of transition-metal dichalcogenides with the layered 1T-CdI_2 structure. Because of their pseudo-two-dimensional character, these materials exhibit interesting physical and chemical properties: intercalation of molecules between layers, superconductivity, and charge density waves, which are known to exist in these materials and which are held responsible for many of their extraordinary electrical transport properties (for a review reference is made to Refs. 4 and 5). At near-stoichiometric compositions the existence of displaced Ti atoms has been suggested, i.e., Frenkel defects consisting of a Ti vacancy and an interstitial in the van der Waals' gap. It turned out that an excess of Ti up to 10% can be accommodated in this gap.

TiS_2 crystals were grown by the vapor phase transport method. Freshly prepared powder was put at the hot end (850 °C) of an evacuated tube. Iodine was used as a transport agent and a small amount of excess S was added to ensure the growth of close to stoichiometric crystals. Chemical analysis confirmed that the crystals were stoichiometric within 1%.

According to the nomenclature presented in Ref. 6, TiS_2 crystallizes in the 1T-CdI_2 structure [space group D^3_{3d} or $P_{\bar{3}m1}$, one Ti at (0,0,0) and two S at (1/3,2/3,1/4) and (2/3,1/3,−1/4)]. The c/a ratio is almost ideal, namely, 1.6691 with $a = 0.3412$ nm and the coordination of the transition metal atom is octahedral.[7] The close packed layers of cations are sandwiched between the two close packed layers of anions. At stoichiometric composition the cations are believed to occupy all the octahedral interstices between two layers of polarized anions. Since the packing of atoms occurs on a hexagonal lattice, the structure of the transition-metal dichalcogenides is usually represented by views on their $(11\bar{2}0)$ planes [see Fig. 1(a)]. Viewed along the c axis, perpendicular to the basal plane, both the S atoms in the outer layer and the Ti atoms in the middle of the first sandwich appear in equal numbers. Consequentially, an image of either Ti or the S atoms would show a sixfold symmetry with 0.34 nm lattice spacing. If both the top S layer and the Ti

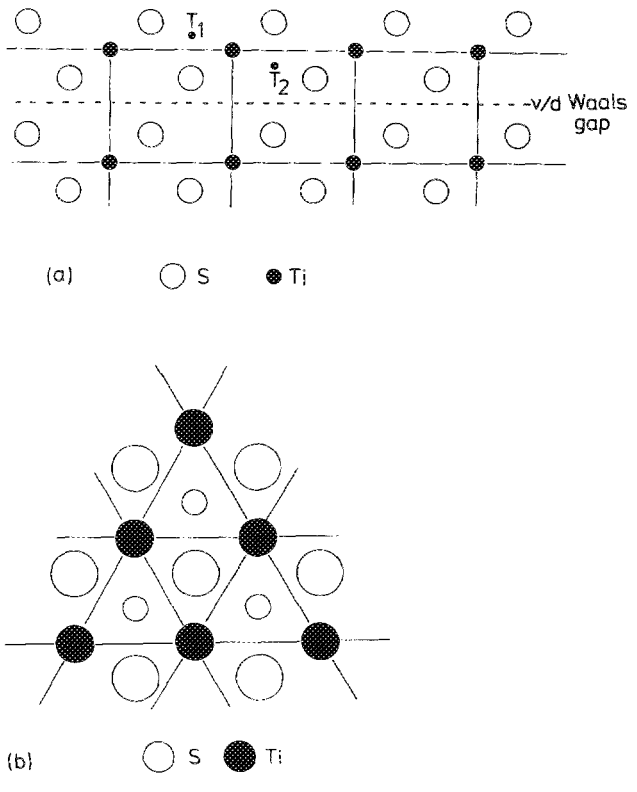

FIG. 1. (a) Second-order prismatic plane $(11\bar{2}0)$ of 1T-TiS_2 structure showing van der Waals gap and stacking order. $T1$ and $T2$ are the two inequivalent tetragonal sites. Solid lines connect the Ti lattice. (b) Basal plane projection of the 1T phase; solid lines connect the Ti lattice.

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layer are visible, then the image will possess threefold symmetry [Fig. 1(b)].

The electronic structure of the transition-metal dichalcogenides roughly exists of rather broad and filled s and p bands and narrow and empty or partly filled transition-metal d states. The current view on TiS_2 is that of a small band-gap semiconductor. The band gap is about 0.3 eV between the S p states and the Ti d states. Because the electrical conductivity of nominally stoichiometric material is metal-like, TiS_2 must be a "dirty" semiconductor. The n-type carriers (from the sign of Hall and Seebeck coefficients) must originate from a large number of intrinsic defects. In Wilson's[5] model some of the p levels are destabilized by the presence of the displaced Ti atoms, so that the corresponding p electrons are transferred back to the d states. Photoelectron spectroscopic results are confusing even more. In a large number of transition-metal dichalcogenides a dispersionless (and therefore localized) state is found close to the Fermi level that is not predicted by band-structure calculations.[8] The highest occupied electronic states are mainly of p character and are directed into the S-Ti-S sandwich layers comprising the TiS_2 lattice. The S 3s orbitals are about 12 eV below the Fermi level whereas the peak in the density of states is about 2.5 eV below E_f.

At relatively small bias voltages tunneling is expected to occur to the states of TiS_2 near the Fermi level. If TiS_2 is indeed an n-type semiconductor, as is generally accepted now, it means that the lower lying d bands of Ti are involved. However, it does not necessarily mean that local maxima correspond to Ti atoms. Since the fresh free surfaces are prepared by cleavage of the comparatively weak vdW bonds, it is most likely that the outer layer at the surface consists of S. Because there exists a substantial covalent mixing between Ti and S($3p$) states and the Ti d bands contain approximately 10% S p orbitals above E_f (Ref. 9) it is most likely that the STM image is showing maxima in the tunneling height associated with electrons at S. As a matter of course the tunneling current at constant height is determined by the probability of electron tunneling between the 6s electron states of tungsten and the electron states of the sample. However, the exact shape of the wave functions of the material outside the material is not known. Therefore, we assume that the conduction electrons are in the vicinity of S atoms in the top layer.

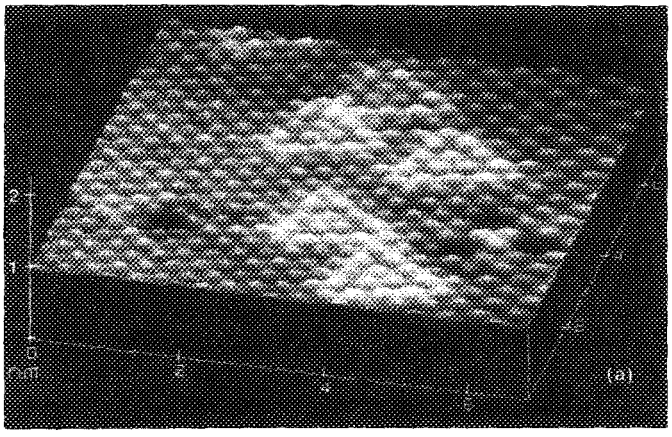
A commercially available STM was used for the imaging of the samples.[10] The samples were cleaved prior to imaging in order to obtain fresh surfaces. The bias voltage applied to the sample was 25 mV with respect to the tip (tip virtually grounded). The tunneling current was locked to 1.3 nA (constant current mode). In Fig. 2 typical STM images of TiS_2 are displayed. Figure 2(a) is a pseudo-3D view and Fig. 2(b) is a top view. The images consist of arrays of bright spots with the expected triangular symmetry separated by 0.34 nm.

As mentioned before the overall symmetry becomes threefold when the second layer containing octahedral sites, occupied by Ti, or the vacant tetrahedral sites in the Ti layer, as designated by T_i in Fig. 1(a), are taken into account. There are still two possibilities: the two hexagons, first of which is centered on S atoms (top layer), are shifted with respect to each other over 1/3 $[\bar{1}100]$ or over 2/3 $[\bar{1}100]$. In the former case the second is centered on Ti (second layer) [Fig. 1(b)]. In the latter case the second is centered on the tetrahedral sites in the Ti layer. Indeed the STM images exhibit the two types of hexagons with different depth as can be seen in Fig. 2(b) and which is displayed more quantitatively by means of a cross-section display in Fig. 3. However, it cannot be concluded from these observations that the hexagonal pattern of black dots is due to the lower lying Ti layer or to the hexagonal pattern of vacant tetrahedral sites lying in the Ti layer.

To solve this question x-ray diffraction has been applied to the STM sample. With the aid of a single-crystal x-ray diffraction technique (Weissenberg) it is possible to distinguish between these two possibilities, because the (hkl) and the $(hk\bar{l})$ spots have different intensities. For instance, if the Ti atoms are chosen to be at the center of a hexagonal unit cell and the S atoms at 2/3,1/3,1/4 and 1/3,2/3, $-$ 1/4 the (011) spot will be weak and the $(01\bar{1})$ spot strong. Using this fact we determined that the Ti atoms correspond to the black dotted regions in the STM image.

The STM images exhibit some striking features which can be grouped into three categories (Fig. 2). Apart from the isolated black holes ("type 1") two other types of more complicated features extending over 6 and 15 sites respectively are randomly distributed over the surface. The "type 6" features consist of a highlighted triangle, in single orientation, of dots enclosed by three black spots. The "type 15" features consist simply of a triangle of 15 highlighted dots also in single orientation. Careful analysis of the type 6 features in a constant height mode shows that the three dark dots surrounding the three bright dots do not correspond to missing atoms but rather with hardly visible atoms. We recall at this point that the Ti atoms are in octahedrally coordinated positions below the S layer. In addition there exist two types of tetrahedrally coordinated sites: one type below each S atom in the top layer and one above each S atom in the bottom layer in the TiS_2 sandwich [Fig. 1(b)]. Based on the x-ray analysis indicating that the hexagonal pattern of black dots in the STM image corresponds to the octahedral site occupied by Ti, the type 15 triangle is centered around an octahedral site and the type 6 triangles are centered around tetrahedral sites.

A supporting argument for this view may be found looking at the mutual densities of the features. Over a total area of about 10^4 surface unit cells the numbers of the various defects were counted. The mean density of type 1, type 6, and type 15 features appeared to be 0.41%, 0.37%, and 0.75%, respectively, i.e., approximately in the ratio 1:1:2. This suggests that the defects are more or less correlated. A plausible explanation would be that during the growth process of the crystals a certain fraction of the Ti atoms is displaced within the sandwich. The two tetrahedral sites in the sandwich are equivalent when considered in the bulk; however, an asymmetry exists when cleaving of the crystal occurs: one of the tetrahedral sites has a S atom on top of it, whereas the other has a triangle of three S atoms above it. Thus the two defects associated with Ti interstitials in tetrahedral sites (type 1



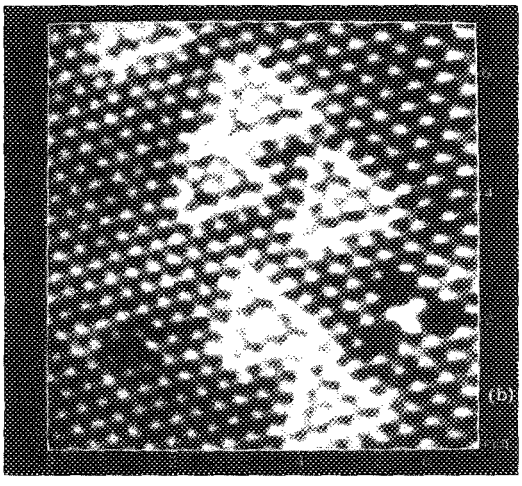


FIG. 2. Constant current map of TiS_2, 300 K, air, $V_{sample} - V_{tip} = 25$ mV, $I_{set} = 1.3$ nA, temperature 300 K. (a) Pseudo-3D view; (b) top view.

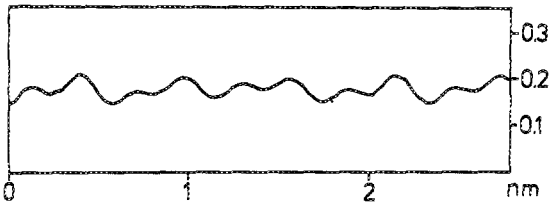


FIG. 3. $(11\bar{2}0)$ cross-section display of tunneling height, showing absence of $(1\bar{1}00)$ first-order prismatic mirror planes necessary for sixfold symmetry.

and type 6) have different appearances but about equal density. They might be considered as "front" and "rear view" of the same defect. Tetrahedral holes in a c.p.h. structure can accommodate spheres of radius $0.225*R$. As a result a Ti atom located in a tetrahedral site right underneath a S atom at the surface may expand the lattice substantially by which the surface atom is pushed out after cleavage. The type 15 defect is then considered to be an octahedral Ti vacancy having the same density as the type 1 and type 6 defect density together.

Point defects may influence the brightness not only at the very site of the defect, but at several neighboring sites as well, as is shown by Mizes and Harrison[11] in the case of a substitutional impurity in graphite. This might be equally true in the case of transition-metal dichalcogenides.

This explanation accounts well for the fact that the imaged sample is of near-stoichiometric composition because it merely describes the displacement of Ti atoms without altering the composition. It also explains why there are no traces of intercalated Ti atoms in the former (before cleavage) vdW gap at the surface. It seems that there is a strong tendency for the sandwich layers to conserve stoichiometric composition, and therefore any excess Ti in nonstoichiometric samples would be stored in the vdW gap as intercalates.

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